Model Validation in Chemical Process with Multiple Steady States

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Pilot plant work is considered a reasonable intermediate step when chemical processes are moved from lab to commercial scale. Using only lab data to design and build a commercial chemical plant is considered risky since limitations that are not present at the smaller scale can become dominant at the larger scale. Mass and heat transfer limitations, for example, play an increasing role during plant scale up. Unfortunately, pilot plants are not easy or cheap to operate and modelers are faced with the problem of getting the most information out of the least expensive pilot plant experimental plan. In the end, pilot plants are viewed more as means to generate product samples for market testing than as devices to use for model validation, despite the great need to have models that can be scaled up reliably.

Complications arise in chemical processes that should be operated in regions of parameter space where two or more equally important, opposing mechanisms compete for control. A well known case is that of strongly exothermic reactions, the opposing mechanisms being heat release by reaction and heat removal by evaporation or by transfer to a cooling fluid. Multicomponent reaction models are also configured often in the form of multiple opposing mechanisms, even under isothermal conditions. Complex dynamic behavior arises in these cases, manifested in the form of multiple steady states, sustained oscillations, and phenomena that is even more exotic, like period doubling bifurcations and chaos. This behavior is often dismissed as being rare or constrained to only a few academic problems, but many important commercial chemical process are affected by it. Olefin polymerization reactions, for example, are some of the most notorious cases. Ignoring such behavior can make control system design difficult at best and even dangerous.

We have developed a kinetic model for a catalytic reaction mechanism using lab scale experiments in an accelerated rate calorimeter, which is a small, non-isothermal, batch reactor capable of holding approximately 5 grams of sample. The main reaction is strongly exothermic and one of the reactants participates also in a side reaction that reduces the activity of the catalyst. The commercial process where this catalyst is going to be used is a continuous one made up of two isothermal reactors in series, of similar residence times, that can be modeled as tank and tubular

reactors, respectively. Under isothermal conditions in a continuously stirred tank reactor, the catalyst exhibits three steady states, one of which is unstable. One of the stable steady states is characterized by lower catalyst activity and, consequently, lower reactant conversion. This state is not only unattractive from an economic perspective, but it is considered unsafe since reactant accumulation increases the chances of reactor runaway episodes. The other stable steady state, corresponding to high catalyst activity and high reactant conversion, is the desired one. Important reactor conditions, like residence time and temperature, will determine the locations of the two points where the reactor switches back and forth between fully ignited (desired) and fully extinct (undesired) conditions. Unfortunately, choosing the operating conditions and the catalyst level that will favor the desired stable steady state is difficult, since process economics demand low catalyst levels and this constraint pushes the system towards the low activity region. In other words, a delicate balance has to be established between process economics and the ability to control the process.

Our kinetic model is now part of steady state reactor models for both the tank and the tubular reactor in the pilot plant. These models have been applied in planning the experimental design used for validation purposes at the pilot plant level, where 10 kilograms of the main reactant are typically converted each hour. The experimental work generated by this design has confirmed the existence of multiple steady states predicted by the tank reactor model and it has been useful in choosing plant start up protocols that avoid the undesired stable steady state. In experiments where the system begins to move away from the desired stable steady state, the insight provided by the model has helped in correcting this situation. A dynamic version of the tank reactor model is also available, and it has been used to analyze the behavior of the plant from start up or transition to new conditions until a new steady state is reached. Comparison of the dynamic model with the results of start up experiments has also provided insight regarding the initial activation of the catalyst, a component of the reaction mechanism that could not be studied during lab experiments. The entire experimental plan has been valuable in fine tuning the parameters of our kinetic model, in preparation for the transition to commercial scale, which will require construction of new facilities based on these reactor models. The ultimate commercial plant will be operated in the same dimensionless parameter region as the pilot plant so it is important to be able to predict and handle complex dynamic behavior.

In this work, we compare the performance of our mechanistic models against that of empirical models obtained by analysis of the chosen statistical experimental design, we point out the potential pitfalls of the empirical models, and we suggest ways around those pitfalls for systems

with complex dynamic behavior. In the absence of a kinetic model for a strongly non-linear system like the one considered in this work, a purely empirical approach to experimental planning and plant scale up is at risk of failing or it has to be constrained to small regions in parameter space where linear approximations are valid and other stable steady states are far enough. Unfortunately, these regions are likely to be of little or no value from a practical viewpoint. The combination of mechanistic and empirical modeling offers a balanced approach. Mechanistic models provide insight that is useful in dealing with complex dynamic behavior, while empirical models allow analysis and optimization of system responses for which mechanistic models are not available.

Our validated reactor models will be used as part of a process intensification strategy that will search for optimum operating conditions of commercial plants and will choose product grade transition strategies for those plants. At the commercial scale, the energy balance plays a more important role and the combination of this balance with the reaction mechanism for the catalyst will introduce complications that process control systems will have to deal with. Those systems should be designed to avoid reaction extinction episodes or the cycling behavior that results from process configurations and process conditions that favor sustained oscillations.